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TESTING OF PLASTIC UTENSILS

POLAROGRAPHIC DETERMINATION OF DI-(2-ETHYLHEXYL)-PHTHALATE AND INVESTIGATION OF THE TENDENCY TO MIGRATION

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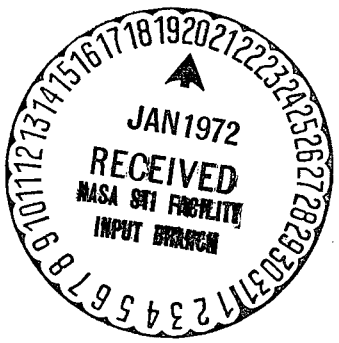

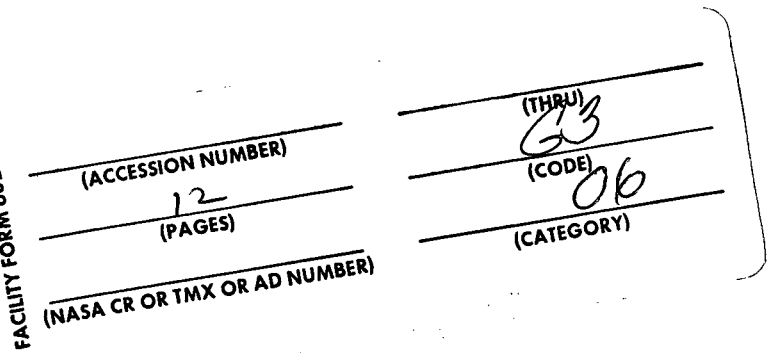

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POLAROGRAPHIC DETERMINATION OF DI-(2-ETHYLHEXYL)-PHTHALATE AND INVESTIGATION OF THE TENDENCY TO MIGRATION

Dr. H. Woggon and U. Koehler

ABSTRACT: Rigid PVC which contains up to 5% di-(2-ethylhexyl)-phthalate as processing aid was to be tested for its sanitary harmlessness for use in food service. (This plasticizer must not be used in West Germany for plastic utensils which come in contact with foodstuffs). A pulse polarographic method was developed with which the smallest amounts of migrating plasticizer could be determined quantitatively. It was shown that the transfer to aqueous as well as alcoholic and fatty foodstuffs of a maximum 3 ppm is tolerably small; as a result, there should be no sanitary objection to the use of DEHP.

Plasticizers are very important as aids in the processing of plastics. /583* However, the use of plasticizer-containing polymers for packaging in the foodstuff industry is only exceptionally possible, particularly for fatty foodstuffs, because of the high solubility of the plasticizers. Particular difficulties are encountered in the determination of plasticizer transfer from plastics with low contents of plasticizer. On the one hand, the concentration of the migrating plasticizer is very slight; on the other hand, other processing aids are transferred, which can markedly disturb the detection and determination of the plasticizer. In general the plasticizer transfer is determined by the weight reduction in the film after the migration. This process, however, is utilizable only for high plasticizer contents and severe plasticizer migration, and even then is connected with very great errors, because the result is obtained as a small difference of two large numbers (film weights).

It is of great interest to be able to determine also small amounts and even traces of plasticizers in foodstuffs, or foodstuff-like model solutions, because

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*Numbers in the margin indicate pagination in the foreign text.

of the increasing use of plastics for packaging of foodstuffs and in connection with the guidelines for the sanitary evaluation of plastic utensils.

The quantitative determination of plasticizer traces directly in foodstuffs is very difficult and practically is possible only with radiochemical methods. Chromatographic procedures haved proved useful for the analysis of plasticizers; gas chromatography in particular [1, 2] has been used for the detection and quantitative determination of these high bailing compounds under particular precautions. Furthermore, IR spectrographic methods [3] are also used for the investigation of plasticizer removal. However, a direct detection with it in the fat or oil used for extraction is not possible.

The polarographic methods known up to the present for the determination of plasticizers, practically all of which are based on the principle of the methods of Whitnack and Gantz [4] are suitable only for the investigation of raw material and not for trace analysis. The introduction of a new polarographic method for the determination DEHP migration therefore signifies a considerable advance in the analysis of plasticizers.

The optimum conditions for the quantitative determination of the smallest amounts of plasticizer were worked out for this method. The polarographic process was compared with the already known thin layer chromatography. The method worked out for DEHP should be applicable for all other phthalate esters.

Experimental Part

Phthalate esters may be determined polarographically directly. Tetraalkylammonium salts are used mostly as conductive electrolytes because of their very negative reduction potentials. The gradation is no longer measurable for very small concentrations, since the polarographic gradation is mostly poorly formed in a strongly negative range of potential. However, when the phthalate ester is nitrated, then the half increment potential is shifted in the positive direction, since the reduction is now confined to the nitro group, which is reduced at -0.4 V. To this may be added that equimolar amounts of nitro compounds yield markedly higher increments and thereby make quantities up to 0.5 μg DEHP/ml measureable.

Nitration

DEHP is converted quantitatively into nitrophthalic acid by nitration with a mixture of equal parts by weight of fuming HNO_3 and concentrated H_2SO_4. The nitration temperature was raised to between 40 and 90°C at intervals by 10 degrees. It was shown that for higher concentrated solutions a nitration time of one hour at 90°C leads to quantitative conversion, while for lower concentrations and equal nitration time a lower temperature is sufficient. The reason for this may be found in the fact that the solubility of the phthalate ester increases with increasing temperature, and only the dissolved component is nitrated (compare Figure 1).

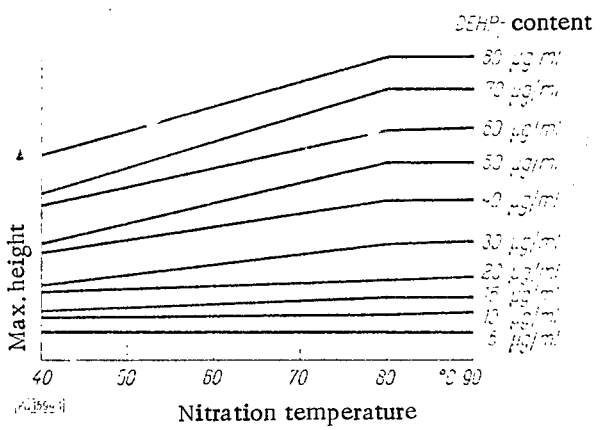

Figure 1. Relation of Maximum Height to Nitration Temperature for Solutions with Variable DEHP Content.

Polarographic Determination

The polarographic determination is made directly in the nitric acid mixture diluted with distilled water, whereby well-formed increments or maxima, are obtained (Figure 2). The half-increment potential amounts to -0.405 V against saturated calomel electrode. The linear concentration relationship was tested from 0.5 to 80 µg DEHP/ml. When the nitration acid is buffered with sodium acetate solution for the polarography, then it is reduced in several single increments with poorly reproducible potentials, whereby the quantitative evaluation is made considerably more difficult. /584

Isolation of the Plasticizer

The sample to be investigated was extracted exhaustively with ether, in general after comminuting, in order to isolate the plasticizer. Here, as well in practical use, other aids are also dissolved out. It is therefore necessary to check whether these compounds would also be converted by the nitration, whereby the polarographic determination would give a misleading result. This occurred with our experimental material for urea derivatives. However, these may be

separated from the phthalate ester before the nitration due to their variable solubility. Monophenyl urea is only slightly soluble in benzene, and practically insoluble in pentane, hexane, and heptane. DEHP on the other hand is very soluble in these solvents. This circumstance was utilized, in that the extraction residues after evaporation of the extraction agent, was dissolved in benzene, whereby a large part of the monophenyl urea remained practically undissolved. Benzene was chosen, because it was best suited as solvent for the thin layer chromatographic determination run in parallel. Aliquot parts of benzene solution can be used for the thin layer chromatographic determination. The monophenyl urea does not disturb this analysis, as could be shown by separately conducted experiments, when a test solution was chromatographed after an addition of monophenyl urea. Aliquot portions of the benzene solution were also removed for the polarographic determination of DEHP and evaporated in the drying oven at 120°C. The residue was taken up in 5 ml pentane, filtered through a G-4 frittered glass, rinsed twice with 2 ml pentane, and the solution again evaporated in the drying oven in a ground glass test tube to dryness. The residue obtained was then nitrated.

Thin-Layer Chromatographic Determination

The method described by H. Piekacz [5] was used for comparison.

For this purpose, plates (20 × 20 cm) were coated with silica gel G (Merck) according to Stahl; the layer thickness was 0.5 mm. The plates are to be activated for 60 min. at 120°C. Methylene chloride serves as medium; the work is carried out in a saturation chamber. The chromatograms are sprayed with a 20% alcoholic vanillin solution, dried 10 min. at 80°C, sprayed with 4N H_2SO_4, and again dried 30 min. at 110°C. DEHP appears as a dark blue spot on a bright background, Rf value 0.46; the limit of detection lies at 1 μg (Figure 3).

Figure 2. Maximum Polarogram of a Nitrated Solution with 5 μg DEHP/ml.

Figure 3. Thin Layer Chromatogram of Heptane Extracts of Coarse Comminuted Rigid PVC. A pure benzene DEHP solution was used for spot comparison.

Directions for Operation

The Leybold Polarograph Model 1954 was used for the tests with frittered glass cell and saturated calomel electrode (drop velocity of the capillaries 2.8 sec) and also a cathode jet polarograph Model K1000 of Southern Analytical Ltd., with polarographic cell after Novak with laterally attached deaeration tube. An ultrathermostat was used.

Solutions and Reagents

Palatinol AH(-di-(2-ethylhexyl) phthalate); nitration acid of equal parts by weight of fuming HNO_3 and concentrated H_2SO_4; 5% urea solution; benzene, analytical; tank nitrogen (washed over pyrogallol and water).

Execution

Alcoholic or benzene solutions of DEHP were prepared for carrying out the calibration curve; the range in concentration was between 50 and 5,000 μg DEHP/ml. One ml of each of these solutions was evaporated in a ground glass test tube (drying oven 120°C). One ml nitric acid is added to the residue and heated 1 hour at 90°C. The mixture is diluted with water, and after addition of 2 ml 5% urea solution, is transferred to a 50 ml graduated flask, and filled with water. After deaeration with nitrogen it is polarographed from 0 to -1.0 V at K1000 with a starting potential of -0.2 V.

According to these directions it is possible to determine as little as 5 μg DEHP/ml test solution, when it is evaluated with the aid of a calibration curve.

For the investigation of plastics, the DEHP is first dissolved in benzene after evaporation of the extracts. An aliquot serves for the thin layer chromatographic determination, a further portion is taken up in 5 ml pentane after

evaporation of the benzene (drying oven 120°C). After filtering the solution through a 12 G-4 frittered glass and rinsing twice with 2 ml pentane, it is dried in a ground glass test tube. This is followed by nitration and further treatment as described above.

Utilization in Analysis of Plastics

PVC products to which a small amount of a plasticizer (maximum 5% DEHP) was added as processing aid were subjected to various use tests. For this purpose, the samples of plastics were brought in contact under various experimental conditions with foodstuff-like model solutions and the DEHP transferred to the solutions were determined.

Six types of rigid PVC of various contents of DEHP (0 to 5%) and about 0.8% /585
monophenyl urea were used for investigation.

Determination of Plasticizer Migration

10 g of the coarse comminuted sample was extracted 5 hrs under reflux with 250 ml solvent (double distilled water, 96% alcohol, ether, and n-heptane) for the determination of the migration of plasticizer under extreme conditions. The noncomminuted plates were brought into contact with 96% alcohol, or n-heptane for 48 hours at 45°C in a ratio of surface: contacting liquid = 1 cm^2: 0.5 ml for the determination under conditions approximating actual practice. The material was then ground under dry ice and screened in order to determine the total content of DEHP in the PVC samples. 1 g of the screened material (granular size is less than 315 μm) was extracted exhaustively with ether in the Soxhlet.

Test for Organoleptic Effects

The comminuted plates were stored for 48 hours at 45°C with each of 100 ml 0.1% NaCl solution, 50% ethanol, and peanut oil. The NaCl solutions were judged by four testers as very slightly to slightly odoriferous, the ethanol as none to very slightly, and the oil as non-odoriferous.

Discussion of Results

It may be seen from the results compiled in Table 1 of the extraction of the coarse comminuted material that there is no detectable plasticizer in the aqueous

extract. The dry content of the aqueous extracts deviates only slightly from the median value of 0.05% for all six samples (0 to 5% DEHP).

TABLE 1. RESULTS OF EXTRACTION OF RIGID PVC WITH VARYING DEHP CONTENTS (SAMPLES REDUCED TO ABOUT 1 CM EDGE LENGTH AND BAILED 5 HOURS UNDER REFLUX)

DEHP Content (%)	Extraction Liquid	Extraction Residue mg/100g PVC	DEHP Content of the Extract (mg/100g PVC)	
			Thin-layer Chromatographic	Polarographic
0	Water	55	-	-
	96% ethanol	13	-	-
	Ether	66	-	-
	Heptane	30	-	-
1	Water	48	-	-
	96% ethanol	55	23	33
	Ether	90	80	81
	Heptane	56	28	33
2	Water	43	-	-
	96% ethanol	57	50	50
	Ether	107	102	111
	Heptane	107	57	56.5
3	Water	49	-	-
	96% ethanol	90	90	87
	Ether	206	240	290
	Heptane	170	100	98
4	Water	47	-	-
	96% ethanol	139	126	116
	Ether	367	336	345
	Heptane	229	120	144
5	Water	62	-	-
	96% ethanol	185	140	144
	Ether	528	400	not analyzed
	Heptane	308	200	194

The plasticizer content increases steadily in the alcoholic extract and reaches nearly 150 mg/100 g PVC for the sample with 5% DEHP. The maximum dry residue of these extracts amounts to 0.2%. The corresponding values of the ether extracts are 400 mg/100g and 0.5%, respectively. The maximum extracted with heptane is 200 mg/100g PVC. Table 2 shows that a detectable plasticizer

migration with ethanol under conditions approximating practice is reached only with a plasticizer content of 3% DEHP. The plasticizer migration increases continuously with increasing DEHP content, and reaches about 150 $\mu g/100cm^2$ surface at 5% DEHP content. 80 μg DEHP/$100cm^2$ were detected in the heptane extract. A comparison with the coarse comminuted material shows that under conditions approximating practice only about 0.3% of the material migrates in alcohol compared to the extraction under more severe conditions. Table 3 gives the results of the exhausting ether extraction.

TABLE 2. RESULTS OF EXTRACTION OF RIGID PVC WITH VARYING DEHP CONTENT (NONCOMMINUTED PLATES OF 10 CM EDGE LENGTH, EXTRACTED 48 HOURS AT 45°C WITH 0.5 ML EXTRACTION LIQUID/CM^2)

DEHP Content (%)	Extraction Liquid	DEHP Content of the Extract			
		(mg/100g PVC)		(mg/$100cm^2$ PVC)	
		Thin-layer Chromatography	Polarographic	Thin-layer Chromatography	Polarographic
0	96% ethanol	-	-	-	-
	Heptane	-	-	-	-
1	96% ethanol	-	-	-	-
	Heptane	-	-	-	-
2	96% ethanol	-	-	-	-
	Heptane	0.032	-	0.010	-
3	96% ethanol	0.096	-	0.028	-
	Heptane	0.064	-	0.019	-
4	96% ethanol	0.373	0.40	0.108	0.116
	Heptane	0.224	0.28	0.065	0.081
5	96% ethanol	0.480	0.496	0.139	0.144
	Heptane	0.160	0.300	0.046	0.083

Inasmuch as it is not to be expected that the theoretical amount of plasticized additive in the formulation could be recovered in a technical product, the values in Table 3 must be considered as real.

A comparison of the extraction values obtained by the two methods gives a satisfactory agreement.

TABLE 3. RESULTS OF EXTRACTION OF RIGID PVC OF VARYING DEHP CONTENT (PULVERIZED MATERIAL WITH GRANULAR SIZE OF 0 TO 315 μM, EXTRACTED 6 HOURS WITH DIETHYL ETHER IN THE SOXHLET)

DEHP Content	Recovered Content of DEHP (%)	
	Thin-Layer Chromatographic	Polarographic
0	-	-
1	1.2	1.06
2	2.0	2.05
3	2.9	2.75
4	3.8	3.8
5	4.4	4.7

Evaluation of the Process

Our results of the investigation may be evaluated as follows: The experimental conditions were so chosen in view of international proposals for evaluation, that 1000 ml solvent in place of 1 kg foodstuff would be brought in contact with 2000 cm^2 contact surface. The extraction value found for DEHP with ethanol is at 150 $\mu g/100cm^2$; this corresponds to a pickup of 3 ppm DEHP in the foodstuff. This amount is extremely slight compared to the Food and Drug Administration of the USA permitted total impurities of 160 ppm; provided that an acute, or chronic toxicity is excluded.

Compared with ethanol, heptane (experiments with edible oil could not be evaluated chromatographically) extracted only about half. Even if heptane does not always show the extraction capacity as much as edible oil, it may still be /586
assumed that edible oil would not take up appreciably greater amounts of DEHP. The organoleptic results are in agreement with this, which at most show slight deviations at the 5% DEHP content level.

According to the FAO/WHO Expert Committee on Food Additives (1962) cited by McCollister [6] the daily intake of 1 mg DEHP per kg body weight for people is considered unobjectionable. For an average body weight of 70 kg the above calculated 3 or 1.5 ppm, respectively, from the extract would thus be considered to be completely tolerable; to which it may be added that it is still questionable whether a person could consume daily 1 kg of such foodstuff.

It follows from this that PVC with 5% DEHP content appears suitable for packaging and storing of aqueous and alcoholic or fatty foodstuffs. Experiments of storage for prolonged periods were not carried out.

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